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(54) **APPARATUS FOR COLLECTING MATERIAL TO BE SPECTRALLY ANALYZED**

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(51) **Int. Cl.**

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G01N 1/00	(2006.01)
A61B 5/00	(2006.01)
A61B 5/1459	(2006.01)
G01N 21/65	(2006.01)
G01N 1/02	(2006.01)

(52) **U.S. Cl.**

CPC ***G01N 1/00*** (2013.01); ***A61B 5/0075*** (2013.01); ***A61B 5/1459*** (2013.01); ***A61B 5/6847*** (2013.01); ***G01N 21/658*** (2013.01); *A61B 2562/028* (2013.01); *A61B 2562/0285* (2013.01); *G01N 1/02* (2013.01); *Y10T 29/49826* (2015.01)

(58) **Field of Classification Search**

USPC 356/301, 72–73

See application file for complete search history.

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Primary Examiner — Abdullahi Nur

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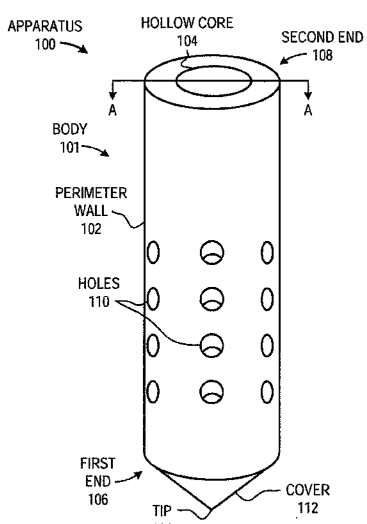
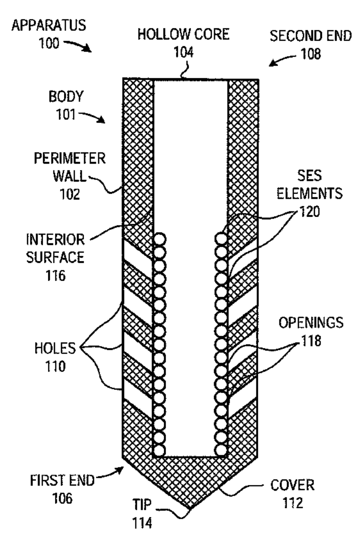
(57) **ABSTRACT**

According to an example, an apparatus for collecting a material to be spectrally analyzed includes a body having a first end and a second end, in which the body is elongated along a first axis from the first end to the second end. The body also includes a hole having an opening formed in an external surface of the body at a location between the first end and the second end and extending at least partially through the body at an angle with respect to the first axis. The body further includes a plurality of surface-enhanced spectroscopy (SES) elements positioned inside the body.

14 Claims, 9 Drawing Sheets





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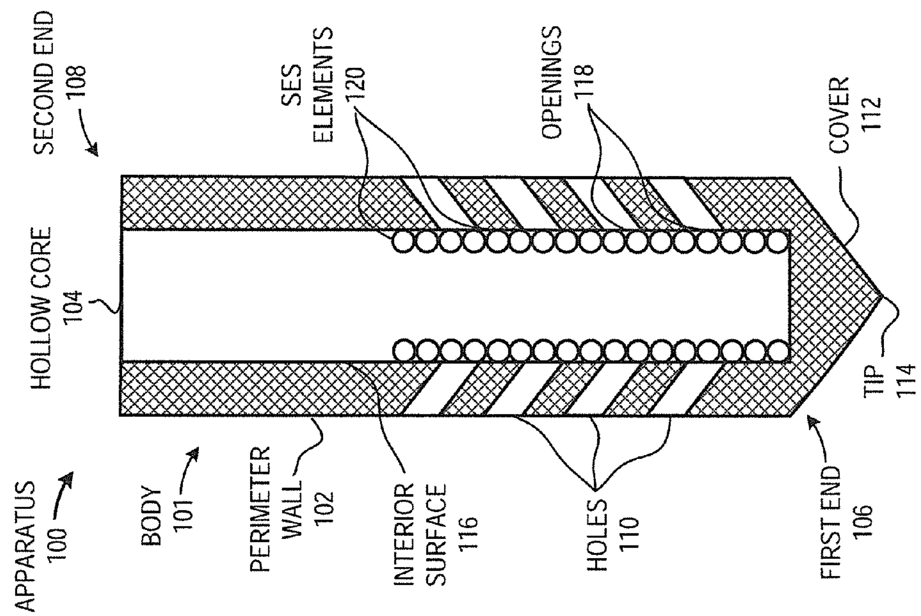
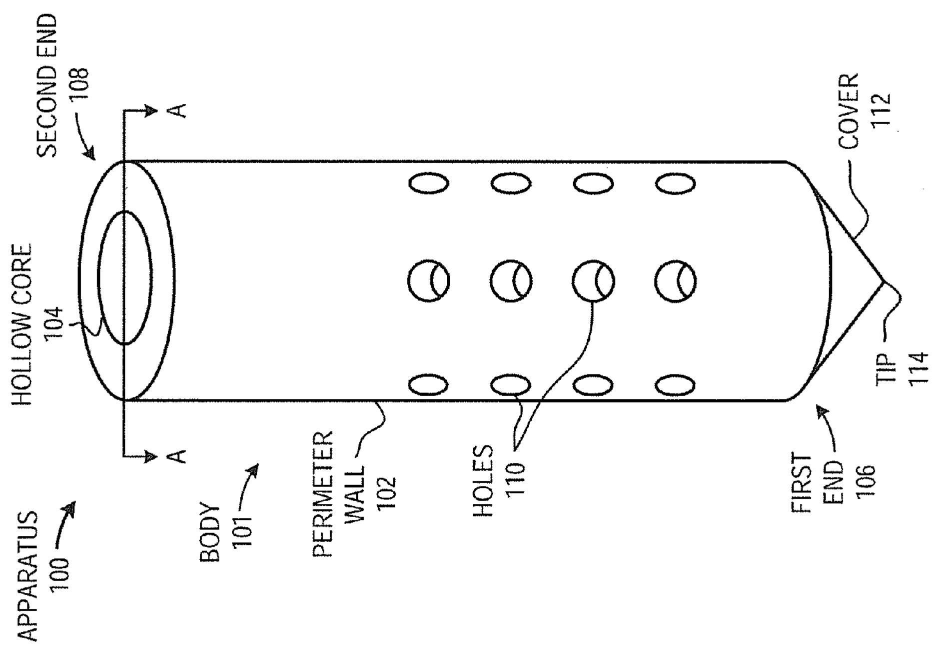


SECOND END 108
HOLLOW CORE 104
SES ELEMENTS 120
OPENINGS 118
COVER 112
APPARATUS 100
BODY 101
PERIMETER WALL 102
INTERIOR SURFACE 116
HOLES 110
FIRST END 106
TIP 114

FIG. 1B



SECOND END 108
A
HOLLOW CORE 104
COVER 112
APPARATUS 100
BODY 101
PERIMETER WALL 102
HOLES 110
FIRST END 106
TIP 114
A

FIG. 1A

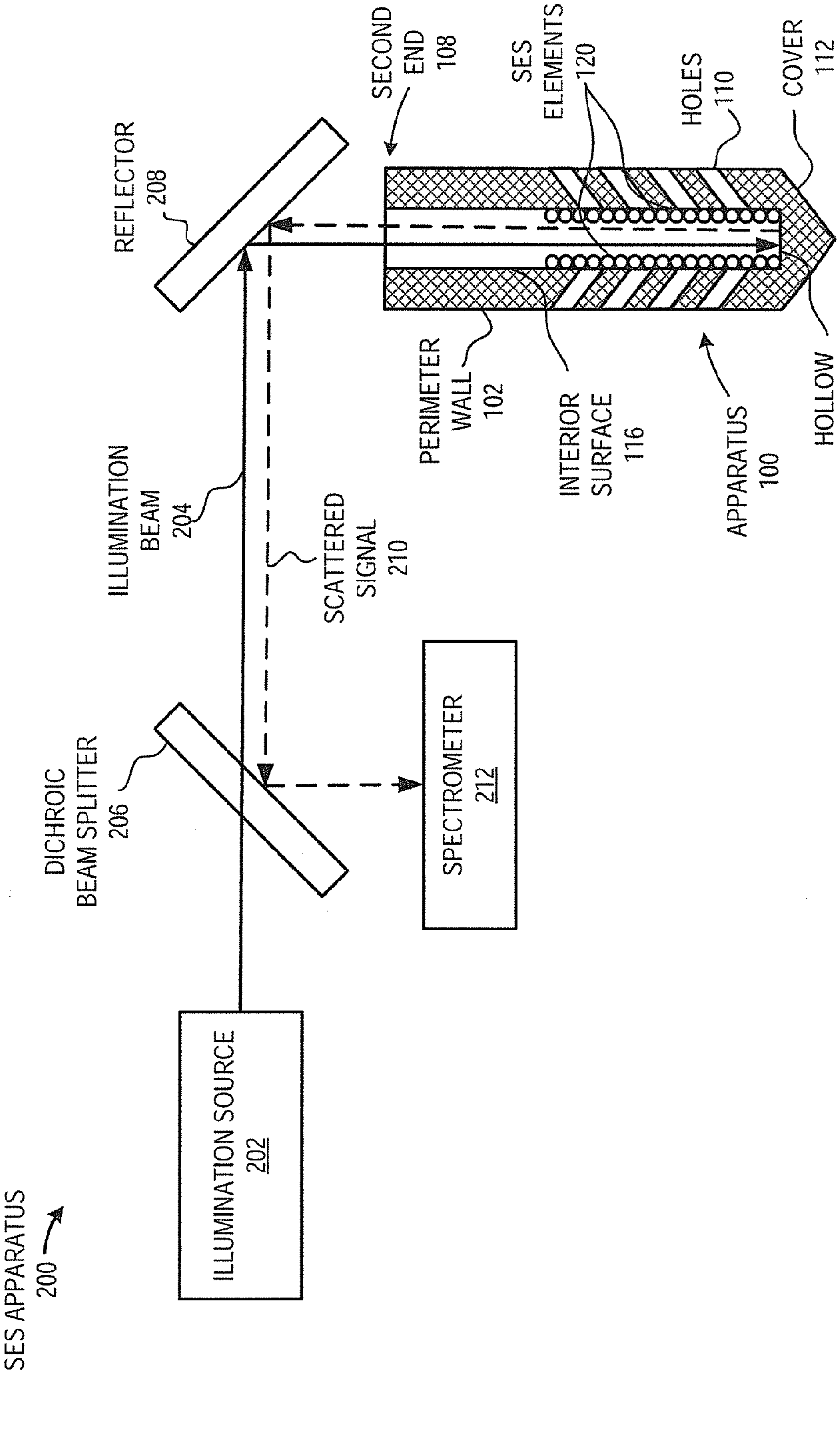

SES APPARATUS 200
ILLUMINATION SOURCE 202
ILLUMINATION BEAM 204
DICHROIC BEAM SPLITTER 206
REFLECTOR 208
SCATTERED SIGNAL 210
SPECTROMETER 212
SECOND END 108
SES ELEMENTS 120
HOLES 110
COVER 112
PERIMETER WALL 102
INTERIOR SURFACE 116
APPARATUS 100
HOLLOW CORE 104

FIG. 2

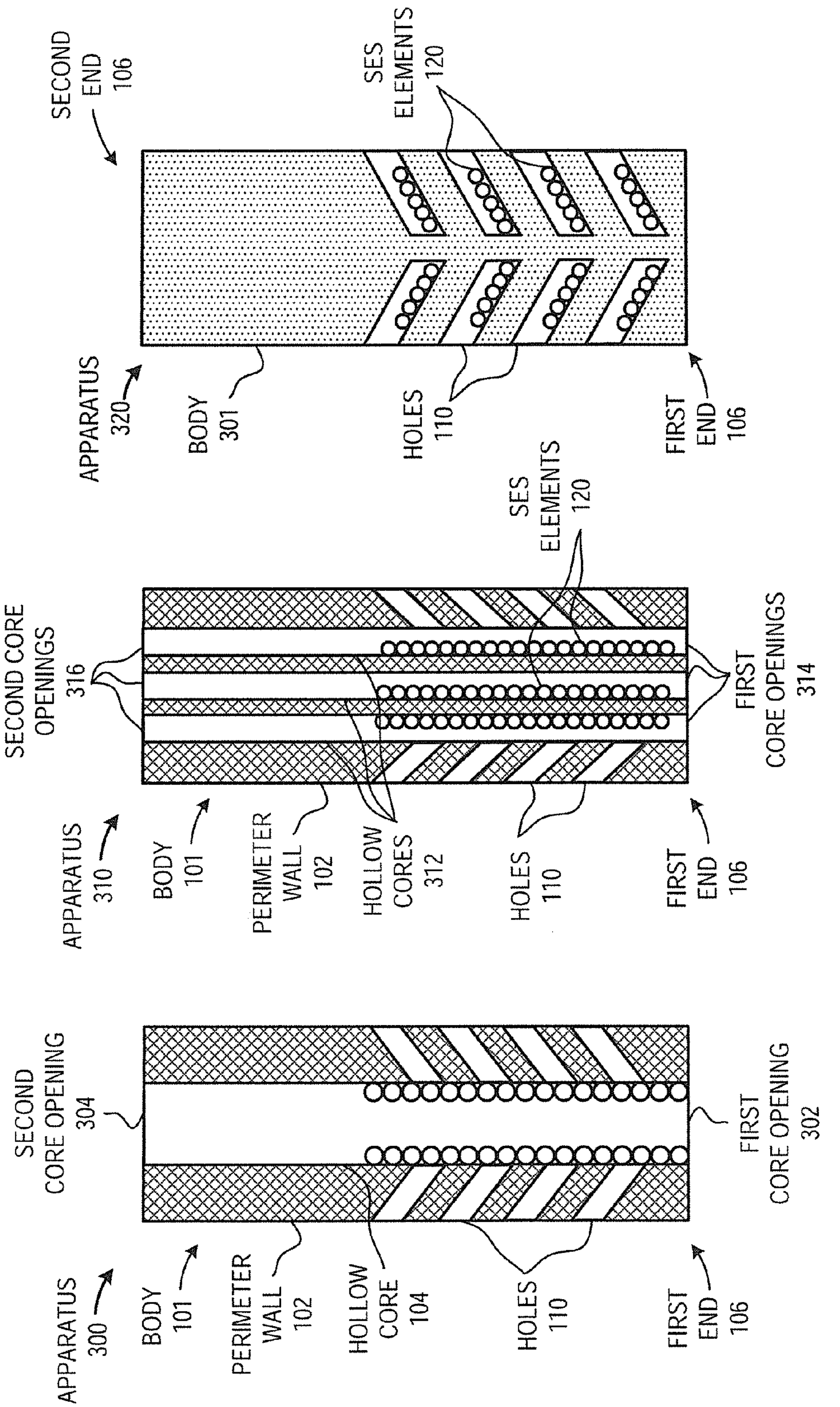


FIG. 3C

FIG. 3B

FIG. 3A

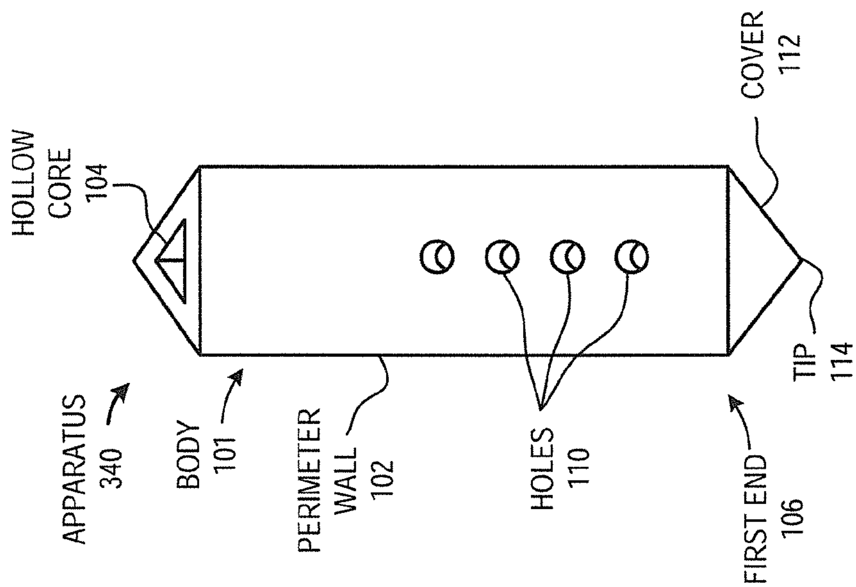
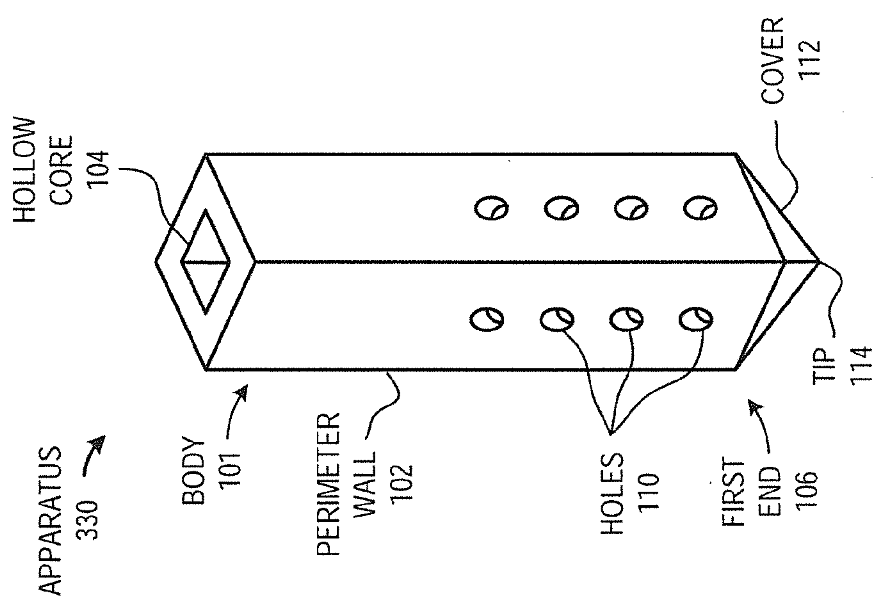

HOLLOW CORE 104
APPARATUS 340
BODY 101
PERIMETER WALL 102
HOLES 110
FIRST END 106
COVER 112
TIP 114

FIG. 3E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APPARATUS 330
BODY 101
PERIMETER WALL 102
HOLES 110
FIRST END 106
COVER 112
TIP 114

FIG. 3D

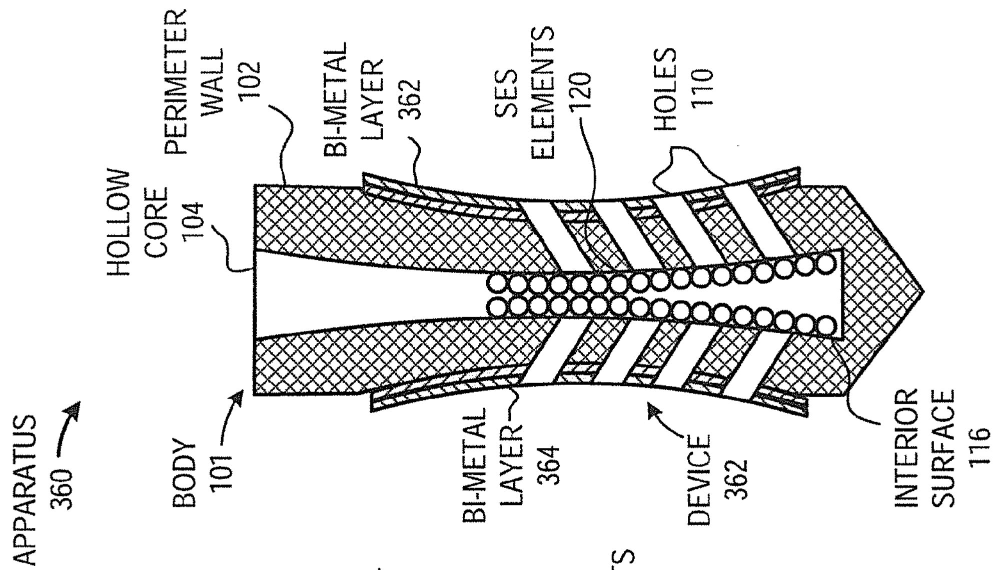

FIG. 3H

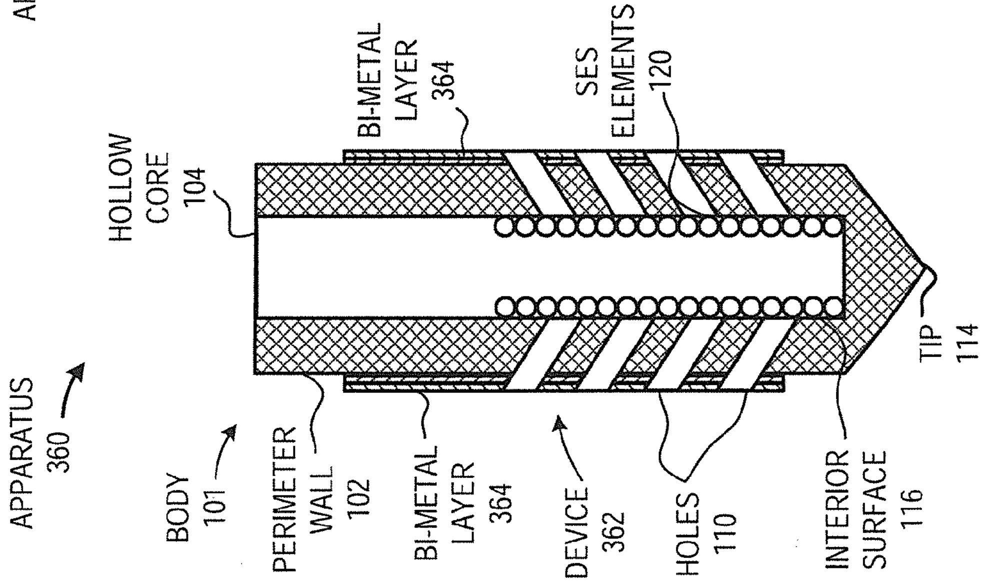

FIG. 3G

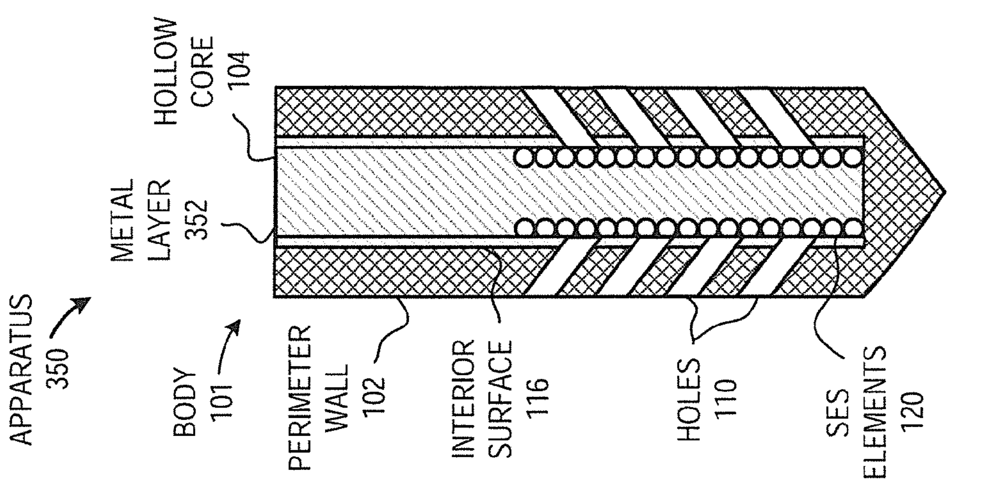

FIG. 3F

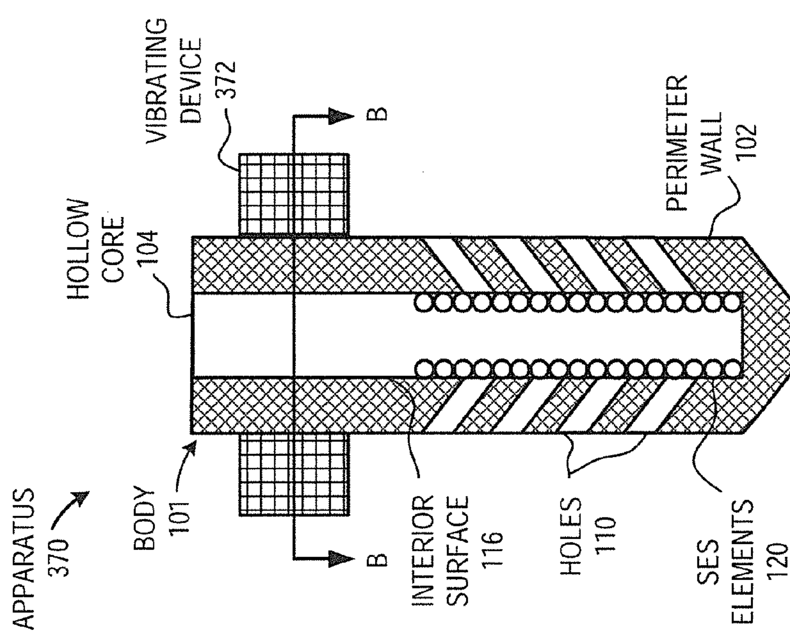
APPARATUS 370
BODY 101
HOLLOW CORE 104
VIBRATING DEVICE 372
B
B
INTERIOR SURFACE 116
HOLES 110
SES ELEMENTS 120
PERIMETER WALL 102

FIG. 3I

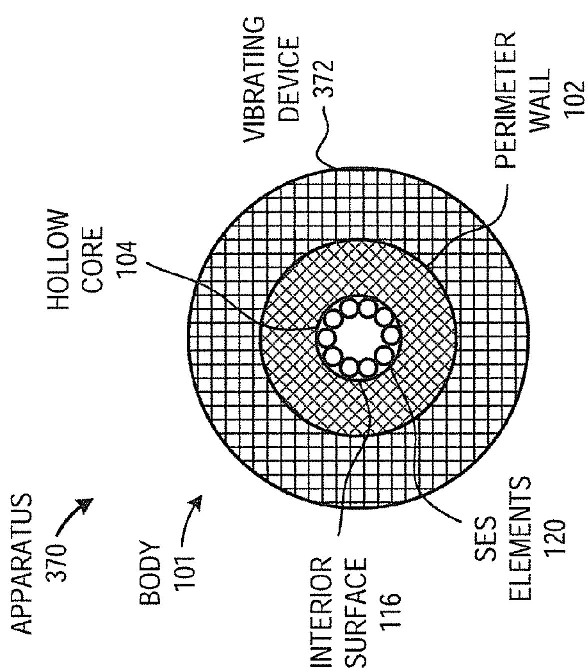
APPARATUS 370
BODY 101
HOLLOW CORE 104
VIBRATING DEVICE 372
PERIMETER WALL 102
INTERIOR SURFACE 116
SES ELEMENTS 120

FIG. 3J

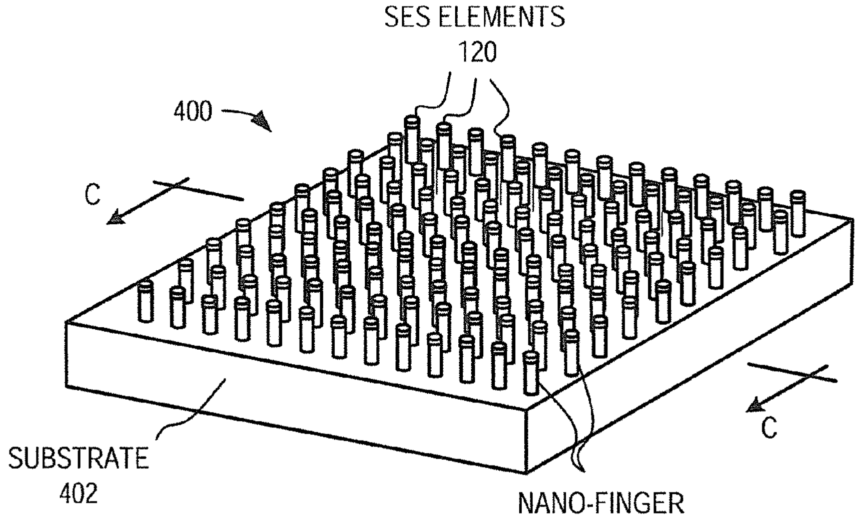

FIG. 4A

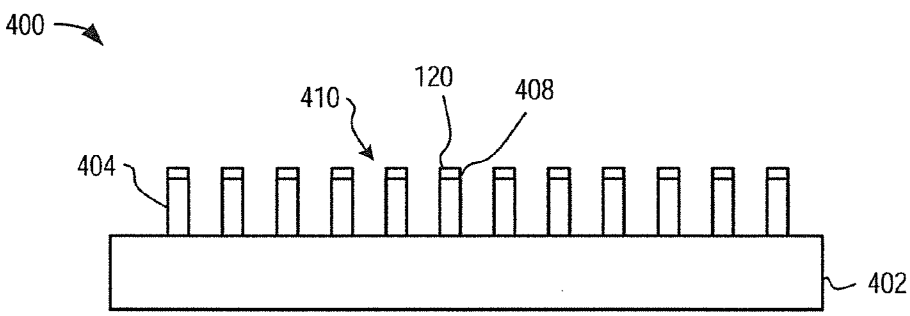

FIG. 4B

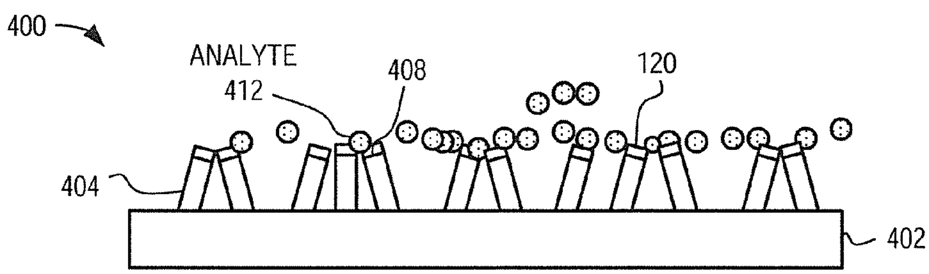

FIG. 4C

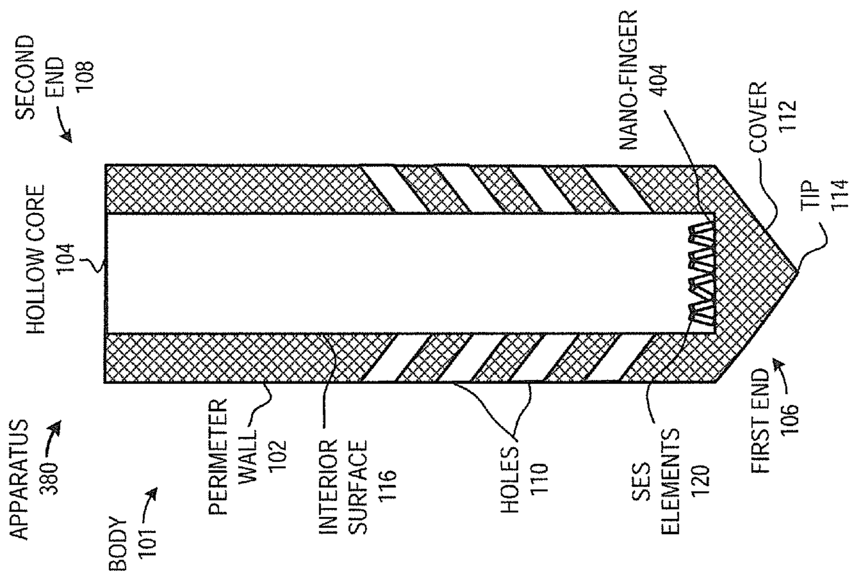
APPARATUS 380
BODY 101
PERIMETER WALL 102
INTERIOR SURFACE 116
HOLES 110
SES ELEMENTS 120
FIRST END 106
HOLLOW CORE 104
SECOND END 108
NANO-FINGER 404
COVER 112
TIP 114

FIG. 4E

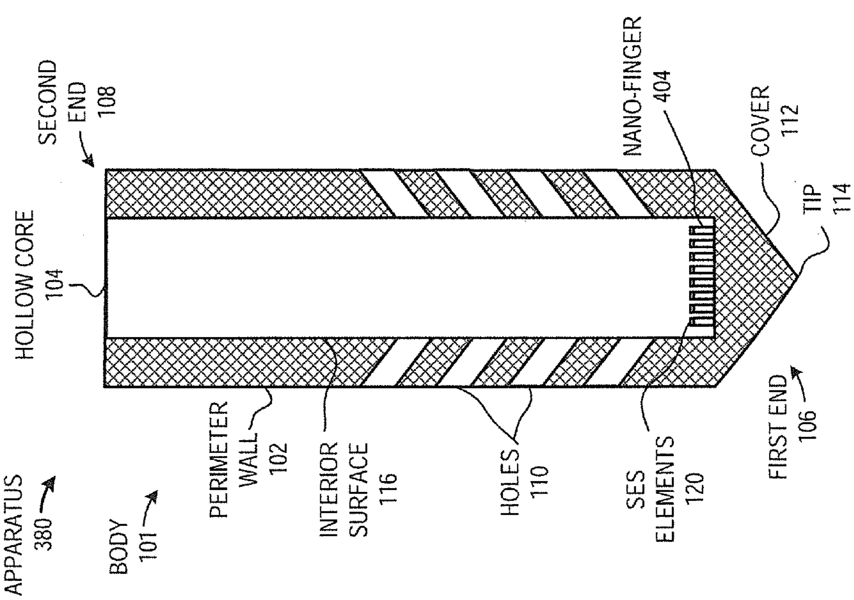
APPARATUS 380
BODY 101
PERIMETER WALL 102
INTERIOR SURFACE 116
HOLES 110
SES ELEMENTS 120
FIRST END 106
HOLLOW CORE 104
SECOND END 108
NANO-FINGER 404
COVER 112
TIP 114

FIG. 4D

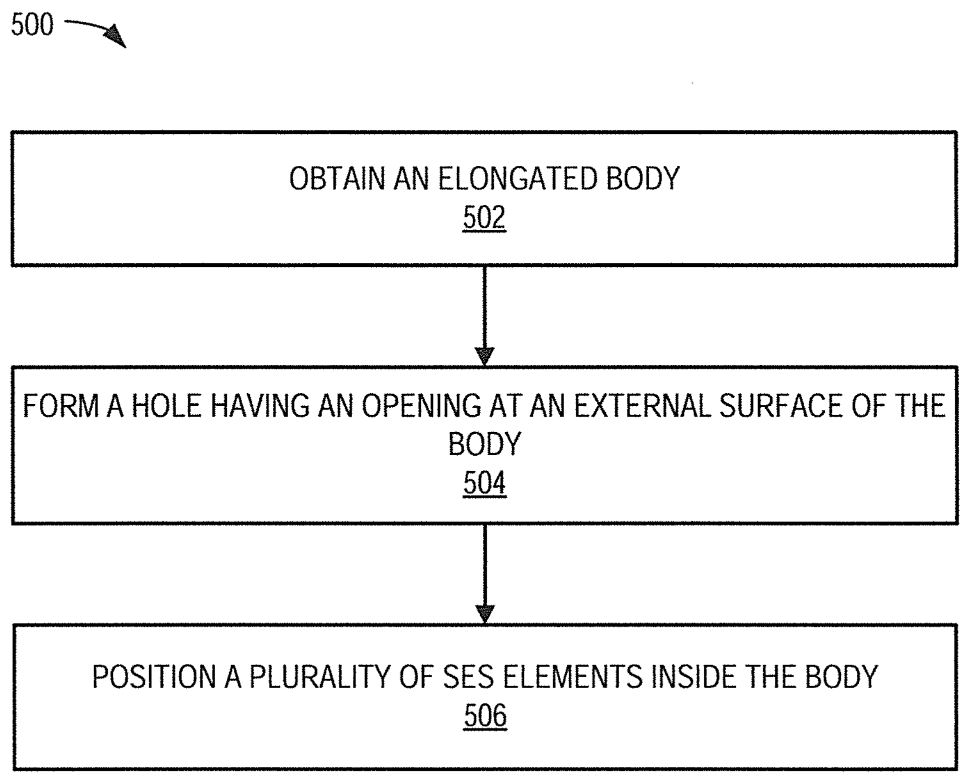
500
OBTAIN AN ELONGATED BODY
502
FORM A HOLE HAVING AN OPENING AT AN EXTERNAL SURFACE OF THE BODY
504
POSITION A PLURALITY OF SES ELEMENTS INSIDE THE BODY
506

FIG. 5

APPARATUS FOR COLLECTING MATERIAL TO BE SPECTRALLY ANALYZED

BACKGROUND

In surface-enhanced spectroscopy (SES), such as surface-enhanced Raman spectroscopy (SERS), vibrationally excitable levels of an analyte are probed. The energy of a photon can shift by an amount equal to that of the vibrational level excited by the photon (Raman scattering). A Raman spectrum, which consists of a wavelength distribution of bands corresponding to molecular vibrations specific to the analyte being probed, may be detected to identify the analyte. In SERS, the analyte molecules are in close proximity, for instance, less than tens of nanometers, to metal nano-particles that may be or may not be coated with a dielectric, such as silicon dioxide, silicon nitride, and a polymer, that, once excited by light, set up plasmon modes, which create near fields around the metal nano-particles. These fields can couple to analyte molecules in the near field regions. As a result, concentration of the incident light occurs at close vicinity to the nano-particles, enhancing the Raman scattering from the analyte molecules.

SERS has recently been performed to probe materials beneath a surface through insertion of an optical fiber having a hollow core containing metal nanoparticles through the surface. Conventional optical fibers have openings at distal ends of the optical fibers for the material to be collected into the hollow core and onto the metal nanoparticles. SERS is then performed on the collected material through application of excitation light onto the metal nanoparticles and materials and detection of Raman scattered light from the materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Features of the present disclosure are illustrated by way of example and not limited in the following figure(s), in which like numerals indicate like elements, in which:

FIG. 1A shows a perspective view of an apparatus for collecting a material to be spectrally analyzed, according to an example of the present disclosure;

FIG. 1B shows a cross-sectional side view of the apparatus taken along lines A-A in FIG. 1A, according to an example of the present disclosure;

FIG. 2 shows a diagram of an apparatus for performing SES, according to an example of the present disclosure;

FIGS. 3A-3C, respectively show cross-sectional side views of an apparatus for collecting a material to be spectrally analyzed, according to examples of the present disclosure;

FIGS. 3D and 3E, respectively show perspective views of an apparatus for collecting a material to be spectrally analyzed, according to examples of the present disclosure;

FIGS. 3F-3I, respectively show cross-sectional side views of an apparatus for collecting a material to be spectrally analyzed, according to examples of the present disclosure;

FIG. 3J shows a cross-sectional top view of an apparatus for collecting a material to be spectrally analyzed along lines B-B in FIG. 3I, according to an example of the present disclosure;

FIG. 4A shows an isometric view of an array of SES elements, in this instance nano-fingers, that may be implemented in the apparatus depicted in FIGS. 1A-3E, according to an example of the present disclosure;

FIGS. 4B and 4C, respectively show cross-sectional views along a line C-C, shown in FIG. 4A, prior to and following collapse of the nano-fingers, according to examples of the present disclosure;

FIGS. 4D and 4E, respectively show cross-sectional side views of an apparatus for collecting a material to be spectrally analyzed, according to another example of the present disclosure; and

FIG. 5 shows a flow diagram of a method for fabricating an apparatus for collecting material from an item of interest to be spectrally analyzed, according to an example of the present disclosure.

DETAILED DESCRIPTION

For simplicity and illustrative purposes, the present disclosure is described by referring mainly to an example thereof. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. It will be readily apparent however, that the present disclosure may be practiced without limitation to these specific details. In other instances, some methods and structures have not been described in detail so as not to unnecessarily obscure the present disclosure.

Throughout the present disclosure, the terms "a" and "an" are intended to denote at least one of a particular element. As used herein, the term "includes" means includes but not limited to, the term "including" means including but not limited to. The term "based on" means based at least in part on. In addition, the term "light" refers to electromagnetic radiation with wavelengths in the visible and non-visible portions of the electromagnetic spectrum, including infrared, near infrared, and ultra-violet portions of the electromagnetic spectrum.

Disclosed herein are an apparatus for collecting a material to be spectrally analyzed and a method for fabricating the apparatus. Also disclosed herein is an apparatus for performing spectroscopy that may implement the material collecting apparatus. The material collecting apparatus disclosed herein may include a body having a first end and a second end, in which the body is elongated along a first axis from the first end to the second end. In addition, a hole having an opening formed in an external surface of the body at a location between the first end and the second end and extending at least partially through the body at an angle with respect to the first axis may be formed in the body. Moreover, a plurality of surface-enhanced spectroscopy (SES) elements may be positioned inside the body.

The material collecting apparatus disclosed herein may be fabricated to be inserted into an item of interest, e.g., a specimen, such as a human, an animal, an insect, a plant, a non-living item, etc. By way of particular example, the item of interest may be a living being and the analyte may be a blood sample, an interstitial fluid sample, a tissue sample, etc. As another example, the item of interest may be a fluid, such as milk. In this example, the analyte may be the fluid itself or molecules, species, compounds, etc., contained in the fluid. As a yet further example, the item of interest may be a fruit, a processed food, etc. Again, the analyte in this example may be a biological and/or chemical species contained beneath the surface of an item of interest.

The material collecting apparatus may be elongated along one axis and may be inserted into the item of interest in a direction that is parallel to the axis. In addition, the material collecting apparatus may collect sample material from the item of interest through the hole, which may traverse the material collecting apparatus in a direction that is substantially transverse to the direction in which the material collecting apparatus is to be inserted into the item of interest. In one regard, therefore, the hole may not be as likely to become clogged by material during insertion of the material collecting apparatus disclosed herein into the item of interest. As such, the material collecting apparatus disclosed herein may afford greater probability of sufficient material to be collected into the apparatus for spectral analysis to be performed on the material.

The material collecting apparatus disclosed herein may be implemented to perform spectroscopy, which is also equivalently referred herein as surface-enhanced spectroscopy (SES), to detect a molecule in an analyte sample collected in the apparatus with a relatively high level of sensitivity. As an example, the material collecting apparatus disclosed herein may be implemented to perform spectroscopy on the collected material while the apparatus is inserted into the item of interest. In another example, the material collecting apparatus disclosed herein may be implemented to perform spectroscopy on the collected material following removal of the apparatus from the item of interest.

With reference first to FIG. **1**A, there is shown a perspective view of an apparatus **100** for collecting a material to be spectrally analyzed, according to an example. It should be understood that the apparatus **100** depicted in FIG. **1**A may include additional components and that some of the components described herein may be removed and/or modified without departing from a scope of the apparatus **100**. It should also be understood that the components depicted in FIG. **1**A are not drawn to scale and thus, the components may have different relative sizes with respect to each other than as shown therein.

As shown in FIG. **1**A, the apparatus **100** may include a body **101**, which in this example includes a perimeter wall **102** surrounding a hollow core **104**, in which the hollow core **104** may be formed by an interior surface of the perimeter wall **102**. The perimeter wall **102** may also include a first end **106** and a second end **108**, in which the second end **108** is positioned at an opposite end of the perimeter wall **102** from the first end **106**. In addition, the perimeter wall **102** may extend along an axis from the first end **106** to the second end **108**.

The perimeter wall **102** may be formed of any reasonably suitable type of material that is of sufficient strength to maintain its shape during insertion of the apparatus **100** into an item of interest. The perimeter wall **102** may be formed of plastic, silver, titanium, composite materials, polymers, silicon, etc. The perimeter wall **102** may also be formed of other materials, such as materials that may be toxic to a specimen.

By way of particular example, the perimeter wall **102** may be a hollow core optical fiber, which may include a photonic crystal or a holey fiber. In this example, the perimeter wall **102** may be an optically transparent material that is surrounded by a cladding (not shown) along the longitudinal axis of the perimeter wall **102**. As another example, the perimeter wall **102** may be formed of an optically reflective material and/or is fabricated such that the interior surface of the perimeter wall **102** is optically reflective. For instance, the interior surface of the perimeter wall **102** may be coated with at least one of a metal, such as gold, silver, TiN (titanium nitride), ZnO (zinc oxide), ITO (indium tin oxide), etc., a protective coating of dielectric material, Bragg layers, etc., to be reflective.

According to an example, the apparatus **100** may have a length that is in the range of about 1 millimeter to 3 centimeters and the body **101** has a maximum diameter across its length (i.e., perpendicular to the axis between the first end **106** and the second end **108**) that is between about 80-500 microns. In another example, the body **101** may have a maximum diameter across its length that is between about 80-150 microns. In addition, the body **101** may have a maximum thickness that is between about 20-200 microns, such that the hollow core **104** has a maximum width across its length of between about 20-150 microns. The diameter of the body **101** may also vary along the length of the body **101**, for instance, such that the first end **106** has a diameter that is smaller than the diameter of the second end **108** of the perimeter wall **102**, vice versa, or a location between the first end **106** and the second end **108** has a wider or smaller diameter than the ends **106**, **108**.

The apparatus **100** may also include a plurality of holes **110** (only two of the holes have been labeled in FIG. **1**A). Although not shown in FIG. **1**A, the holes **110** may be provided at spaced intervals along the entire periphery of the perimeter wall **102**. In any regard, the plurality of holes **110** are depicted as extending from an exterior surface of the perimeter wall **102** and into the hollow core **104**. In this regard, when the apparatus **100** is inserted into a surface of an item of interest, material contained in the item of interest may flow through the holes **110** and into the hollow core **104**. The material may flow into the hollow core **104** through capillary forces. Other manners in which the material may flow into the hollow core **104** as well as the configurations of the holes **110** are described in greater detail with respect to FIG. **1**B below.

The apparatus **100** may also include a cover **112** that blocks an opening in the hollow core **104** at the first end **106** of the perimeter wall **102**. The cover **112** is further depicted as including a pointed tip **114**, which may facilitate insertion of the apparatus **100** into an item of interest. The cover **112** may be integrally formed with the perimeter wall **102** or may be attached to the first end **106** of the perimeter wall **102** through use of an adhesive, welding, etc.

Turning now to FIG. **1**B, there is shown a cross-sectional side view of the apparatus **100** taken along lines A-A in FIG. **1**A, according to an example. As more clearly shown in FIG. **1**B, each of the holes **110** is angled with respect to the axis at which the perimeter wall **102** extends. Particularly, the holes **110** are angled such that the openings of the holes **110** at the exterior of the perimeter wall **102** may be at a relatively larger distance from the first end **106** as compared with the openings of the holes **110** at the interior of the perimeter wall **102**. In addition, the holes **110** may extend through the entire width of the perimeter wall **102**, to thereby expose the hollow core **104** to the external environment through the perimeter wall **102**. In this regard, material from an item of interest may be collected into the hollow core **104** through the holes **110**.

Also shown in FIG. **1**B are a plurality of surface-enhanced spectroscopy (SES) elements **120** positioned in the hollow core **104**. SES may include surface-enhanced Raman spectroscopy (SERS), surface-enhanced luminescence detection, surface-enhanced fluorescence detection, or other types of surface-enhanced optically enhanced detection. Although not shown, SES elements **120** may additionally or alternatively be provided in the holes **110** of the apparatus **100**. In any regard, the SES elements **120**, which may include signal enhancing elements, such as plasmonic nano-particles, nanowires, or other signal enhancing structures, are depicted as being arranged in various ordered or random configurations along an interior surface **116** of the perimeter wall **102**. Although not shown, the SES elements **120** may be provided around the circumference of the interior surface **116**. In addition, although SES elements **120** have been depicted as being positioned over openings **118** in the interior surface **116** of the holes, the SES elements **120** may be cleared from the openings **118**. Thus, for instance, the holes **110** may be formed in the perimeter wall **102** following deposition of the SES elements **120** and the SES elements **120** located at the openings **118** may be removed during or following formation of the holes **110**. In addition, or alternatively, the SES elements **120** may be positioned in the hollow core **104** with sufficient spaces between the SES elements **120** to enable analyte collected through the holes **110** to pass between the SES elements **120** positioned at the openings **118** of the holes **110**.

The SES elements **120** may one or both of enhance signal scattering and facilitate analyte adsorption. The SES elements **120** may generally enhance sensing operations, such as, surface enhanced Raman spectroscopy (SERS), enhanced photoluminescence, enhanced fluorescence, etc., to be performed on molecules positioned on or near the SES elements **120**. In some examples, the SES elements **120** may be functionalized to facilitate adsorption of analyte molecules. For example, surfaces of the SES elements **120** may be functionalized such that a particular class of analytes is attracted and may bond or be preferentially adsorbed onto the SES elements **120**.

According to an example, the SES elements **120** include elements, such as plasmonic nanoparticles or nanostructures, which may include plasmon-supporting materials such as but not limited to, gold (Au), silver (Ag), and copper (Cu). The SES elements **120** may have nanoscale surface roughness, which may generally be characterized by nanoscale surface features on the surface of the layer(s) and may be produced spontaneously during deposition of the plasmon-supporting material layer(s). By definition herein, a plasmon-supporting material is a material that facilitates signal scattering and the production or emission of a signal from an analyte on or near the material during spectroscopy. In addition, the SES elements **120**, e.g., plasmonic nanostructures, may be deposited into the hollow core **104** through, for instance, physical vapor deposition (PVD), chemical vapor deposition (CVD), sputtering, etc., of metallic material, or self-assembly of pre-synthesized nano-particles. Alternatively, the SES elements **120** may be deposited onto a substrate (not shown), for instance, of a polymer material, a metallic material, a semiconductor material, etc., and the substrate may be inserted into the hollow core **104**. According to a particular example, the SES elements **120** are positioned on tips of nano-fingers as discussed in greater detail below with respect to FIGS. **4**A-**4**C.

Turning now to FIG. **2**, there is a diagram of an apparatus **200** for performing SES, according to an example. It should be understood that the apparatus **200** depicted in FIG. **2** may include additional components and that some of the components described herein may be removed and/or modified without departing from a scope of the apparatus **200**. It should also be understood that the components depicted in FIG. **2** are not drawn to scale and thus, the components may have different relative sizes with respect to each other than as shown therein.

As shown in FIG. **2**, the apparatus **200** may include the apparatus **100** for collecting a material to be spectrally analyzed depicted in FIGS. **1**A and **1**B. The apparatus **200** may also include an illumination source **202**, which may emit a beam of illumination **204** (such as a laser beam, an LED beam, or other type of light beam) through a dichroic beam splitter **206**. The apparatus **200** is may further include a reflector **208** that is to reflect the illumination beam **204** into the material collecting apparatus **100** to illuminate the SES elements **120** and analyte molecules contained in the material collecting apparatus **100**. In this regard, the apparatus **200** may be implemented following collection of the analyte molecules from an item of interest through the holes **110**.

Generally speaking, the illumination beam **204** operates as an excitation light on the SES elements **120**, which causes near fields around the SES elements **120** to be created. The near fields around the SES elements **120** may couple to analyte molecules (not shown) in the vicinities of the SES elements **120**. The metallic nanoparticles (or other plasmonic structures) of the SES elements **120** may also act to enhance the signal emission, e.g., Raman emission, process of the analyte molecules. As a result, scattered light (or other signal) is emitted from the analyte molecules and the emission of the scattered signal **210** is enhanced by the SES elements **120**. A portion of the scattered signal **210**, which may be emitted in all directions from the analyte molecules near the SES elements **120**, may be emitted toward the reflector **208**.

According to an example, and as discussed above, the interior surface **116** of the perimeter wall **102**, which may also include an interior surface of the cover **112**, may be reflective. In this example, the interior surface **116** may enable greater intensities or flux of the illumination beam **204** to be applied onto the SES elements **120** and the scattered signal **210** emitted from the analyte molecules to be directed out of the apparatus **100**.

In any regard, the scattered signal **210** may be reflected from the reflector **208** and back to the dichroic beam splitter **206**. The dichroic beam splitter **206** may also reflect a portion of the scattered signal **210** toward a spectrometer **212**. The spectrometer **212** may include optical elements, such as, slits, gratings, lenses, etc., that allow for the separation and measurement of different wavelengths of light. The spectrometer **212** may also include a detector, e.g., a photomultiplier tube (PMT), a charge-coupled device (CCD), a complementary metal-oxide-semiconductor (CMOS), etc., detector) to measure the intensities of the separated wavelength bands. The measured intensities of the separated wavelength bands may be used to identify the analyte.

Various modifications may be made to the apparatus **200** depicted in FIG. **2** without departing from a scope of the apparatus **200**. For instance, the reflector **208** may have a parabolic shape that is to focus the illumination beam **204** into the hollow core **104** of the perimeter wall **102** and/or to focus the scattered signal **210** onto the dichroic beam splitter **206**. As another example, instead of or in addition to the use of the reflector **208**, an optical fiber (not shown) may be connected to the second end **108** of the apparatus **100** and positioned to receive from and direct light to the dichroic beam splitter **206**. In this example, the optical fiber may be connected to the second end **108** of apparatus **100** through use of a fastener, e.g., a sleeve, or the optical fiber may be fused to the second end **108**. As a yet further example, various additional optical components, e.g., mirrors, prisms, etc., may be positioned to direct the illumination beam **204** into the hollow core **104** and/or the scattered signal **210** to the spectrometer **212**.

Additionally, various modifications may be made to the material collecting apparatus **100** depicted in FIGS. **1**A, **1**B, and **2** without departing from a scope of the apparatus **100** depicted therein. Examples of the modifications to the material collecting apparatus **100** are depicted herein with respect to the diagrams of the apparatuses depicted in FIGS. **3**A-**3**J. Although the apparatuses depicted in FIGS. **3**A-**3**J are discussed as including various features, it should be clearly understood that the various features depicted therein may be combined in any of multiple combinations without departing to a scope of the apparatus **100** disclosed herein.

With reference first to FIG. **3**A, there is shown a cross-sectional side view of an apparatus **300** for collecting a material to be spectrally analyzed, according to an example. The apparatus **300** may include all of the features of the apparatus **100** depicted in FIG. **1**B, except for the cover **112** at the first end **106** of the perimeter wall **102**. Instead, in the apparatus **300** in FIG. **3**A, the hollow core **104** may include a first core opening **302** and a second core opening **304**. In one regard, when the apparatus **300** is inserted into an item of interest, material from the item of interest may be collected into the hollow core **104** through the first core opening **302**. In addition, if the first core opening **302** becomes blocked or impeded, material from the item of interest may still be collected into the hollow core **104** through the holes **110**.

With reference now to FIG. **3**B, there is shown a cross-sectional side view of an apparatus **310** for collecting material to be spectrally analyzed, according to another example. The apparatus **310** is depicted as including all of the features of the apparatus **100** depicted in FIG. **3**A, except that the apparatus **310** may include a plurality of hollow cores **312**. According to an example, each of the hollow cores **312** may have circular cross-sections similar to the hollow core **104** depicted in FIG. **1**B, and may include a first core opening **314** and a second core opening **316**. The hollow cores **312** may also include SES elements **120**. In addition, the holes **110** may extend through the perimeter wall **102** and into respective ones the hollow cores **312** to introduce analyte material into close proximities to the SES elements **120**.

According to another example, a hollow core **312**, such as a centrally located hollow core **312**, may not be in communication with any of the holes **310**. In this example, the hollow core **312** that is not in communication with any of the holes **310** may still receive material from an item of interest through a first core opening **314** of that hollow core **312**. According to a further example, the first end **106** of the apparatus **310** may include a cover **112** as shown in FIG. **1**B.

Turning now to FIG. **3**C, there is shown a cross-sectional side view of an apparatus **320** for collecting a material to be spectrally analyzed, according to another example. The apparatus **320** may differ from the apparatus **100** depicted in FIGS. **1**B, **3**A, and **3**B in that the apparatus **320** may not include a hollow core. Instead, the body **101** the apparatus **320** may be formed of a material through which light may relatively easily traverse. That is, the body **301** may be formed of an optically transparent material. In addition, the SES elements **120** may be positioned within the holes **110** in the apparatus **320**. In this regard, excitation light may be pumped through the body **301** and onto the SES elements **120** contained in the holes **110**.

According to an example, an opaque and/or reflective cladding (not shown) may be provided on an exterior surface of the body **301** to increase the intensity and flux of the excitation light being directed onto the SES elements **120** and the scattered signals emitted from molecules in contact with and/or close proximities to the SES elements **120**. In addition, or alternatively, the apparatus **320** may include a cover **112** as shown in FIG. **1**B.

Turning now to FIGS. **3**D and **3**E, there are respectively shown perspective views of apparatuses **330** and **340** for collecting material to be spectrally analyzed, according to other examples. The apparatuses **330** and **340** are similar to the apparatus **100** depicted in FIG. **1**A, but have different cross-sectional shapes as compared to the apparatus **100**. That is, the apparatus **330** is depicted as having a square or rectangular cross-section and the apparatus **340** is depicted as having a triangular cross-section. As other examples, however, the apparatus for insertion into an item of interest may include other cross-sectional shapes, such as other polygon shapes, ovals, etc. The apparatus **100** may also have different widths along the longitudinal and/or axial directions, such that the apparatus has a non-uniform cross-section in either or both of the longitudinal and axial directions of the apparatus **100**.

Turning now to FIG. **3**F, there is shown a cross-sectional side view of an apparatus **350** for collecting a material to be spectrally analyzed, according to another example. The apparatus **350** may differ from the apparatus **100** depicted in FIG. **1**B in that the apparatus **350** may include an electrically conductive metal layer **352** on the interior surface **116** of the perimeter wall **102**. Particularly, the electrically conductive metal layer **352** is depicted as being provided between the SES elements **120** and the interior surface **116**. The electrically conductive metal layer **352** may be provided on the interior surface **116** through any suitable metal deposition technique. For instance, the electrically conductive metal layer **352**, which may include Au (gold), Pt (platinum), TiN (titanium oxide), etc., may be deposited using atomic layer deposition (ALD), or other suitable deposition technique. In addition, the electrically conductive metal layer **352** may be a relatively thin coating, for instance, anywhere in the range between about 10 nm-100 nm.

Generally speaking, the electrically conductive metal layer **352** is to generate an electric field through receipt of a voltage, in which the electric field is to enhance attraction of analytes onto the SES elements **120**. Although not shown, the electrically conductive metal layer **352** may be divided into separate segments, in which different segments may receive differently biased voltages, such that the electric field may be generated between the different segments of the electrically conductive metal layer **352**.

Turning now to FIGS. **3**G and **3**H, there are shown cross-sectional side views of an apparatus **360** for collecting a material to be spectrally analyzed, according to another example. The apparatus **360** may differ from the apparatus **100** depicted in FIG. **1**B in that the apparatus **360** may include a device **362** positioned on the body **101** to controllably reduce a diameter of the body **101**. The device **362** may have a pair of bi-metal layers **364**, one on each side of the perimeter wall **102**. Although not shown, each of the bi-metal layers **364** may wrap around part of the outer circumference of the perimeter wall **102**. In this regard each of the bi-metal layers **364** may have curved configurations that substantially match the curvature of the perimeter wall **102**.

The bi-metal layers **364** may be fabricated on the perimeter wall **102** through any suitable metal deposition techniques. For instance, the bi-metal layers **364** may be fabricated through evaporation of metals on either side of the perimeter wall **102**. In addition, a first layer of each of the bi-metal layers **364** may be formed of a material that has a different thermal coefficient than the second layer of each of the bi-metal layers **364**. More particularly, the different thermal coefficients of the first layers and the second layers of each of the bi-metal layers **364** may cause the bi-metal layers **364** to be bent when heat is applied to the bi-metal layers **364**. An example of this bending is depicted in FIG. **3**H. As shown therein, the bending of the bi-metal layers **364** may generally cause the body **101** to be compressed. In addition, as the bi-metal layers **364** cool down, the body **101** may return to the decompressed configuration depicted in FIG. **3**G.

Thus, for instance, the apparatus **360** may be inserted into an item of interest while in the compressed state depicted in FIG. **3**H. Following insertion of the item of interest, the bi-metal layers **364** may cool down thus causing the body **101** of the apparatus **360** to return to the decompressed configuration depicted in FIG. **3**G. In one regard, therefore, as the bi-metal layers **364** cool down, the pressure inside of the hollow core **104** may increase due to the expansion of the size of the hollow core **104**. This increased pressure may enhance collection of the material into the specimen through the holes **110**.

Turning now to FIGS. **3**I and **3**J, there are respectively shown a cross-sectional side view of an apparatus **370** for collecting a material to be spectrally analyzed and a cross-sectional top view of the apparatus **370** taken along lines B-B in FIG. **3**I, according to another example. The apparatus **370** may differ from the apparatus **100** depicted in FIG. **1**B in that the apparatus **370** may include a vibrating device **372** in contact with the body **101**. Particularly, the vibrating device **372** depicted in FIGS. **3**I and **3**J may be provided around the body **101**.

According to an example, the vibrating device **372** may be formed of a lead zirconate titanate (PZT) material that displays a piezoelectric effect when supplied with a voltage. In one regard, the vibrating device **372** may vibrate the apparatus **370** to enhance penetration of the apparatus **370** into an item of interest and to assist in the collection of analyte through the holes **110**.

Turning now to FIGS. **4**A-**4**C, there are respectively shown an isometric view and side views of an array **400** of SES elements **120**, according to an example. It should be understood that the array **400** depicted in FIGS. **4**A-**4**C may include additional components and that some of the components described herein may be removed and/or modified without departing from a scope of the apparatus for insertion into a surface of an item of interest disclosed herein. It should also be understood that the components depicted in FIGS. **4**A-**4**C are not drawn to scale and thus, the components may have different relative sizes with respect to each other than as shown therein.

Generally speaking, the array **400** depicted in FIGS. **4**A-**4**C includes an example in which the SES elements **120** may be positioned on the tops of nano-fingers **404**. As shown in FIG. **4**A, the array **400** includes a substrate **402** upon which the nano-fingers **404** extend. More particularly, the nano-fingers **404** may be attached to and extend above a surface of the substrate **402**. The substrate **402** may be formed of any suitable material, such as, silicon, silicon nitride, glass, plastic, polymer, SiO_2, Al_2O_3, aluminum, etc., or a combination of these materials, etc.

According to an example, the nano-fingers **404** may have dimensions that are in the nanometer range, for instance, dimensions that may be less than about 500 nm, and may be formed of a relatively flexible material to enable the nano-fingers **404** to be laterally bendable or collapsible, for instance, to enable tips of the nano-fingers **404** to move toward each other, as discussed in greater detail herein below. Examples of suitable materials for the nano-fingers **404** include polymer materials, such as, UV-curable or thermal curable imprinting resist, polyalkylacrylate, polysiloxane, polydimethylsiloxane (PDMS) elastomer, polyimide, polyethylene, polypropelene, polyurethane, fluoropolymer, etc., or any combination thereof, metallic materials, such as, gold, silver, aluminum, etc., semiconductor materials, etc., and combinations thereof.

The nano-fingers **404** may be attached to the surface of the substrate **402** through any suitable attachment mechanism. For instance, the nano-fingers **404** may be grown directly on the substrate **402** surface through use of various suitable nano-structure growing techniques. As another example, the nano-fingers **404** may be integrally formed with the substrate **402**. In this example, for instance, a portion of the material from which the substrate **402** is fabricated may be etched or otherwise processed to form the nano-fingers **404**. In a further example, a separate layer of material may be adhered to the substrate **402** surface and the separate layer of material may be etched or otherwise processed to form the nano-fingers **404**. In various examples, the nano-fingers **404** may be fabricated through a nanoimprinting or embossing process in which a template of relatively rigid pillars may be employed in a multi-step imprinting process on a polymer matrix to form the nano-fingers **404**. In these examples, a template may be formed through photolithography or other advanced lithography with the desired patterning to arrange the nano-fingers **404** in the predetermined arrangement. More particularly, for instance, the desired patterns may be designed on a mold by any of E-beam lithography, photolithography, laser interference lithography, Focused Ion Beam (FIB), self-assembly of spheres, etc. In addition, the pattern may be transferred onto another substrate, for instance, a silicon, glass, or polymer substrate (PDMS, polyimide, polycarbonate, etc.). Various other processes, such as, etching, and various techniques used in the fabrication of micro-electromechanical systems (MEMS) and nano-electromechanical systems (NEMS) may also be used to fabricate the nano-fingers **404**.

The nano-fingers **404** have been depicted as having substantially cylindrical cross-sections. It should, however, be understood that the nano-fingers **404** may have other shaped cross-sections, such as, for instance, rectangular, square, triangular, etc. In addition, or alternatively, the nano-fingers **404** may be formed with features, such as, notches, bulges, etc., to substantially cause the nano-fingers **404** to be inclined to collapse in particular directions. Thus, for instance, two or more adjacent nano-fingers **404** may include the features to increase the likelihood that the nano-fingers **404** at least partially collapse toward each other. Various manners in which the nano-fingers **404** may be collapsed are described in greater detail herein below.

The array **400** may include a substantially random distribution of nano-fingers **404** or a predetermined configuration of nano-fingers **404**. In any regard, according to an example, the nano-fingers **404** may be arranged with respect to each other such that the tips of at least two neighboring nano-fingers **404** may be able to be brought into close proximity with each other when the nano-fingers **404** are in a partially collapsed state. By way of particular example, the neighboring nano-fingers **404** may be positioned less than about 100 nanometers apart from each other. According to a particular example, the nano-fingers **404** may be patterned on the substrate **402** such that neighboring ones of the nano-fingers **404** preferentially collapse into predefined geometries, for instance, triangles, squares, pentagons, etc.

In addition, although FIG. **4**A depicts the array **400** as having a relatively large number of nano-fingers **404** arranged along each row, it should be understood that the array **400** may include any number of nano-fingers **404** in each row. In one regard, a relatively large number of nano-fingers **404** may be provided on the substrate **402** to generally enhance the likelihood of detectable light emissions from molecules of an analyte.

The SES elements **120** may include a plasmonic material such as, but not limited to, gold, silver, copper, platinum, aluminum, etc., or a combination of these metals in the form of alloys, or other suitable material that may be able to support surface plasmons for field enhancement for signal scattering. In addition, the SES elements **120** may be multilayer structures, for example, 10 to 100 nm silver layer with 1 to 50 nm gold over-coating, or vice versa. By definition herein, a plasmonic material is a material that supports plasmons. The SES elements **120** may also include other nanostructures and nanoparticles that are coated with a plasmonic material such as metal. In these examples, the SES elements **120** may include, for instance, gold and silver colloidal nanoparticles, black silicon coated with Au or Ag, etc.

Turning now to FIG. **4**B, there is shown a cross-sectional view along a line C-C, shown in FIG. **4**A, of the array **400**, in accordance with an example. As shown therein, each of the tips **408** of the nano-fingers **404** may include a respective SES element **120** disposed thereon. The SES elements **120**, which may be metallic nanoparticles, may be deposited onto the tips **408** of the nano-fingers **404** through one of, for instance, physical vapor deposition (PVD), chemical vapor deposition (CVD), sputtering, etc., of metallic material, or self-assembly of pre-synthesized nano-particles.

Although the nano-fingers **404** have been depicted in FIGS. **4**A-**4**B as each extending vertically and at the same heights with respect to each other, it should be understood that some of the nano-fingers **404** may extend at various angles and heights with respect to each other. The differences in angles and/or heights between the nano-fingers **404** may occur, for instance, due to differences arising from manufacturing or growth variances that may be existent in the fabrication of the nano-fingers **404** and the deposition of the SES elements **120** on the nano-fingers **404**, etc.

As shown in FIG. **4**B, the nano-fingers **404** may be in a first position, in which the tips **408** are in a substantially spaced arrangement with respect to each other. The gaps **410** between the tips **408** may be of sufficiently large size to enable a liquid to be positioned in the gaps **410**. In addition, the gaps **410** may be of sufficiently small size to enable the tips **408** of at least some of the nano-fingers **404** to be drawn toward each other as the liquid provided in the gaps **410** evaporates, through, for instance, capillary forces applied on the tips **408** as the liquid evaporates.

Turning now to FIG. **4**C, there is shown a cross-sectional view along a line C-C, shown in FIG. **4**A, of the array **400**, following evaporation of the liquid, according to an example. The view depicted in FIG. **4**C may be identical to the view depicted in FIG. **4**B, except that the nano-fingers **404** may be in a second position, in which the tips **408** of some of the nano-fingers **404** have been drawn toward with each other. According to an example, the tips **408** of some of the nano-fingers **404** may be in and may remain in relatively close proximity to with each other for a period of time due to the capillary forces applied on adjacent ones of the nano-fingers **404** during and following evaporation of the liquid (not shown) in the gaps **410** between the tips **408**. In addition, the SES elements **120** on the adjacent tips **408** may bond to each other through, for instance, gold-gold bonding, binding molecules (not shown), etc.

In any event, and in one regard, the tips **408** of the nano-fingers **404** may be caused to be drawn toward each other as shown in FIG. **4**C to enhance signal emission by analyte molecules **412** in the near fields of the SES elements **120** because the relatively small gaps between the SES elements **120** on the adjacent tips **408** create "hot spots" having relatively large electric field strengths. According to an example, the nano-fingers **404** may be positioned into the partially collapsed state depicted in FIG. **4**C prior to insertion of the apparatus **100** into a surface of an item of interest.

According to an example, the SES elements **120** depicted in FIGS. **4**A-**4**C may be formed on the substrate **402** and the substrate **402** may be inserted into the apparatus **100**. For instance, the array **400**, including both the SES elements **120** and the substrate **402**, may be inserted into the hollow core **104** and/or the holes **110** of the apparatus **100**. The array **400** may also be attached to an interior surface of the perimeter wall **102**, for instance, through use of an adhesive.

In another example, the SES elements **120** depicted in FIGS. **4**A-**4**C may be formed directly on an interior surface **116** of the perimeter wall **102** (and/or the holes **110**) instead of first being formed on the substrate **402**. In this example, the perimeter wall **102** may include a material and structure that is able to be in a relatively flat state and a relatively curved state. As such, the SES elements **120** may be formed on the perimeter wall **102** while the perimeter wall **102** is in the relatively flat state and the perimeter wall **102** may be caused to obtain the relatively curved state following formation of the SES elements **120**. The perimeter wall **102** in this example may be formed of a material and structure that is to automatically move from the relatively flat state to the relatively curved state to application of an external stimulus, which may include a chemical stimulus, an electrical stimulus, a thermal stimulus, a physical stimulus, etc. Examples of materials that may be used to form the perimeter wall **102** may include titanium-palladium-nickel, nickel-titanium-copper, gold-cadmium, iron-zinc-copper-aluminium, titanium-niobium-aluminium, uranium-niobium, hafnium-titanium-nickel, iron-manganese-silicon, nickel-titanium, nickel-iron-zinc-aluminium, copper-aluminium-iron, titanium-niobium, zirconium-copper-zinc, nickel-zirconium-titanium, etc.

Turning now to FIGS. **4**D and **4**E, there are shown cross-sectional side views of an apparatus **380** for collecting a material to be spectrally analyzed, according to another example. The apparatus **380** may differ from the apparatus **100** depicted in FIG. 1B in that in the apparatus **380**, a plurality of nano-fingers **404** may be positioned on a bottom of the interior surface **116**. The bottom of the interior surface **116** may be a side of the cover **112** that is opposite the tip **114** on the cover **112**. The nano-fingers **404** may be positioned on the bottom of the interior surface **116** or alternatively, the top of the cover **112**, in any of the manners discussed above with respect to FIG. **4**A. In addition, the SES elements **120** may be positioned on tops of nano-fingers **404**. By way of example, the nano-fingers **404** and the SES elements **120** may be provided on the cover **112** and the cover **112** may then be attached to the body **101**.

Moreover, the nano-fingers **404** are depicted in FIG. **4**E as being in a partially collapsed configuration such that some of the SES elements **120** are in contact with other SES elements **120** as discussed above with respect to FIG. **4**C. In one regard, when the SES elements **120** positioned on the nano-fingers **404** are illuminated, a radiation pattern may be formed that is relatively sharp, directional, and couples well to the optical modes of the apparatus **380**, which may substantially enhance the signal emitted out of the apparatus **380**. According to an example, the bottom of the interior surface **116** may have an optically reflective surface as discussed above, to also enhance the radiation pattern formed above the SES elements **120**.

Turning now to FIG. **5**, there is shown a flow diagram of a method **500** for fabricating an apparatus **100** for collecting material from an item of interest to be spectrally analyzed, according to an example. It should be understood that the method **500** depicted in FIG. **5** may include additional processes and that some of the processes described herein may be removed and/or modified without departing from a scope of the method **500**. In addition, although particular reference is made herein to the apparatus **100** as being fabricated through implementation of the method **500**, it should be understood that the method **500** may be implemented to fabricate a differently configured apparatus, such as any of the other apparatuses **300**, **310**, **320**, **330**, and **340** disclosed herein, without departing from a scope of the method **500**.

At block **502**, a body **101** having a first end **106** and a second end **108**, in which the body **101** is elongated along a first axis from the first end **106** to the second end **108** may be obtained. The body **101** may include a perimeter wall **102**, in which the interior surface **116** of the perimeter wall **102** may form a hollow core **104** as shown, for instance, in FIGS. **1**A and 1B. Alternatively, the body **101** may include a solid structure as shown, for instance, in FIG. **3**C. In addition, the body **101** may include any of a variety of cross-sectional shapes as also discussed above with respect to FIGS. **3**A-**3**E. As a further alternative, the body **101** may include a relatively flat or curved configuration that is to be folded or curled such that a surface the body **101** forms a hollow core **104**.

At block **504**, a hole **110** (or holes **110**) may be formed, in which the hole(s) **110** may have an opening at an external surface of the body **101** at a location between the first end **106** and the second end **108** and may extend at least partially through the body **101** at an angle with respect to the first axis. According to an example, the hole(s) **110** may be formed to have an opening **118** at the interior surface **116** of the perimeter wall **102**, for instance, as shown in FIG. **1**B. According to another example, the hole(s) **110** may be formed such that an end of the hole(s) **110** opposite the opening at the external surface of the body **101** is closed, for instance, as shown in FIG. **3**C. In either example, the hole(s) **110** may be formed such that the opening(s) of the hole(s) **110** opposite the opening(s) at the external surface of the body **101** is in closer proximity to the first end **106** than the opening(s) at the external surface of the body **101**.

The hole(s) **110** may be formed in the body **101** through implementation of any suitable fabrication technique. For instance, the hole(s) **110** may be formed in the body **101** through use of etching techniques, drilling techniques, etc.

At block **506**, a plurality of SES elements **120** may be positioned inside the body **101**. The SES elements **120** may be positioned inside the body **101** through any of the manners discussed above. In addition, the SES elements **120** may be positioned in either or both of a hollow core **104** and the hole(s) **110** of the body **101**. According to an example, the SES elements **120** may be positioned inside of the hollow core **104** prior to formation of the hole(s) **110** in the perimeter wall **102** at block **504**. In this example, the openings in the SES elements **120** may be formed to enable analyte material to be introduced into the hollow core **104** through the hole(s) **110**.

In an example in which the body **101** may include a relatively flat or curved configuration that is to be folded or curled, the SES elements **120** may be positioned on a surface of the body **101** prior to the body **101** being folded or curled. In addition, the hole(s) **110** may be formed in the body **101** at any time during the fabrication of the apparatus **100**. The apparatus **100** may additionally be fabricated to include any of the additional features discussed above.

Although described specifically throughout the entirety of the instant disclosure, representative examples of the present disclosure have utility over a wide range of applications, and the above discussion is not intended and should not be construed to be limiting, but is offered as an illustrative discussion of aspects of the disclosure.

What has been described and illustrated herein is an example along with some of its variations. The terms, descriptions and figures used herein are set forth by way of illustration only and are not meant as limitations. Many variations are possible within the spirit and scope of the subject matter, which is intended to be defined by the following claims—and their equivalents—in which all terms are meant in their broadest reasonable sense unless otherwise indicated.

What is claimed is:

1. An apparatus for collecting a material to be spectrally analyzed, said apparatus comprising:

a body having a perimeter wall and a hollow core, said perimeter wall having a first end and a second end;

a cover positioned on the first end of the perimeter wall to block an end of the hollow core, said cover having a conical tip extending away from the perimeter wall and a reflective surface on a side of the cover opposite the conical tip, wherein the body is elongated along a first axis from the first end to the second end and wherein the conical tip is to be inserted through a surface of an item of interest;

a hole having a first opening formed in an external surface of the perimeter wall and a second opening formed at an interior of the perimeter wall, wherein the second opening is closer to the first end of the perimeter wall than the first opening; and

a plurality of surface-enhanced spectroscopy (SES) elements positioned inside the hollow core.

2. The apparatus according to claim **1**, wherein the hollow core is formed by an interior surface of the perimeter wall and extends along the first axis.

3. The apparatus according to claim **2**, wherein the hollow core extends from the first end to the second end of the body.

4. The apparatus according to claim **2**, wherein the plurality of SES elements are positioned in the hole, the hollow core, or both the hole and the hollow core.

5. The apparatus according to claim **2**, further comprising:

a metal layer provided on the interior surface of the perimeter wall, wherein the metal layer is to receive a voltage to enhance attraction of an analyte onto the SES elements.

6. The apparatus according to claim **1**, wherein the body has a maximum diameter perpendicular to the first axis of between about 80-500 microns.

7. The apparatus according to claim **1**, further comprising:

a device positioned on the body to controllably reduce a diameter of the body.

8. The apparatus according to claim **1**, further comprising:

a vibrating device in contact with the body to cause the body to vibrate.

9. The apparatus according to claim **1**, wherein the perimeter wall surrounds a plurality of hollow cores, wherein each of the plurality of hollow cores extends along the first axis, and wherein the second opening connects to at least one of the plurality of hollow cores.

10. The apparatus according to claim **1**, wherein the body is formed of an optically transparent material.

11. The apparatus according to claim **1**, further comprising:

a plurality of nano-fingers extending from a surface inside of the body, wherein the plurality of SES elements are positioned on tips of the plurality of nano-fingers.

12. An apparatus for performing surface-enhanced spectroscopy (SES), said apparatus comprising:

a probe having,

a body having perimeter wall and a hollow core, said perimeter wall having a first end and an opposite a second end;

a cover positioned on the first end of the perimeter wall to block an end of the hollow core, said cover having a conical tip extending away from the perimeter wall and a reflective surface on a side of the cover opposite the conical tip, wherein the body is elongated along a first axis from the first end to the second end and wherein the conical tip is to be inserted through a surface of an item of interest;

a hole having an a first opening formed in an external surface of the perimeter wall and a second opening formed at an interior of the perimeter wall, wherein the second opening is closer to the first end of the perimeter wall than the first opening; and

a plurality of surface-enhanced spectroscopy (SES) elements positioned inside the hollow core;

an illumination source in communication with the second end of the body to illuminate the plurality of SES elements; and

a detector positioned to detect light emitted from an analyte positioned near the plurality of SES elements.

13. The apparatus according to claim **12**, wherein the hollow core is formed by an interior surface of the perimeter wall and extends along the first axis from the first end to the second end of the body.

14. A method for fabricating an apparatus for collecting material from an item of interest to be spectrally analyzed, the method comprising:

obtaining a body having a perimeter wall and a hollow core, said perimeter wall having a first end and a second end;

a cover positioned on the first end of the perimeter wall to block an end of the hollow core, said cover having a conical tip extending away from the perimeter wall and a reflective surface on a side of the cover opposite the conical tip, wherein the body is elongated along a first axis from the first end to the second end and wherein the conical tip is to be inserted through a surface of an item of interest;

forming a hole having a first opening at an external surface of the perimeter wall and a second opening formed at an interior of the perimeter wall, wherein the second opening is closer to the first end of the perimeter wall than the first opening; and

positioning a plurality of surface-enhanced spectroscopy (SES) elements inside the hollow core.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 9,097,616 B2
APPLICATION NO. : 13/750848
DATED : August 4, 2015
INVENTOR(S) : Shih-Yuan Wang et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Claims:

In column 14, line 61, in Claim 12, delete "an a" and insert -- a --, therefor.

Signed and Sealed this
Twenty-first Day of June, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office